HOLAPPA'S 'LIQUID WINDOW' REVISITED*

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Abstract
Theoretical thermodynamic calculations to determine the boundaries of the 'liquid window' (region containing only *liquid* oxide phase in equilibrium with liquid steel) were carried out in order to understand the thermodynamic conditions associated with clogging of the submerged entry nozzle during the continuous casting of steels. This work, limited to the system Fe-Al-Ca-O-S, repplicating a similar paper from the literature, was done using the same steel with the following chemical composition:0.35%C, 0.25%Si and 0.50%Mn. The 'margins' of the 'liquid window' were modified by oxygen (20 to 40 ppm), sulfur (50-250 ppm) and aluminum (100-400 ppm) content, as well as by the temperature (1550-1600 °C). Aim of this work is to remake the fundamental part of the computational calculations made by Holappa *et al.*, this time using modern thermodynamic software and databases, with the firm intention to stimulate students at the undergraduate level to include computer assisted thermodynamics in their advanced studies.
Keywords: 'Liquid window'; inclusions; steel refining; thermodynamics.

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1 INTRODUCTION

At a recent stage in the history of the steel industry, the notion of 'inclusion engineering' has been introduced, which synthesizes the study of the best ways to reduce the number or obtain inclusions with properties more favorable to the applications of steel products. According to Costa e Silva [1], effective 'inclusion engineering' involves three steps: (a) a good knowledge of how inclusions influence properties, (b) understanding what is the effect of each type of inclusions on these properties and thus which is the most desirable inclusion in a given product and (c) adjusting the processing parameters to obtain these inclusions.

The potential of thermodynamics as a tool for understanding and modeling phenomena belonging to this area of engineering is significant – thus it has been under use for a long time; the works of Königsberger *et al.* [2], Frank[3], and Oertel and Costa e Silva [4], for example, give testimony of this in a very comprehensive way. Although these authors have already used graphical representations, it is in a research article in 2003 from Holappa *et al.*[5] that a significant use of this type of results is made.

Holappa and coworkers carry out a thermodynamic evaluation of inclusion formation and modification in calcium treated steel from ladle to tundish and mold until steel solidification. In their work they tested and applied both general software packages as well as an interactive software called ICA. The thermodynamic software (ChemSage program and databases with a quasichemical slag phase model from GTT Technologies, Germany) was used to calculate equilibrium formation of oxides and sulphides; theICA program package was created especially for the project, to calculate, interactively and stepwise, steel solidification and inclusion formation/transformation occurring in the residual liquid fraction.

Main question addressed in their work was, the understanding of the thermodynamic conditions associated with clogging of the tundish valve during the continuous casting of steels. Nozzle blockage problems were encountered since the beginning of the continuous casting technique (in the 1960s) and the analysis of blocked nozzles revealed that the main reason for the blockages was deposition of solid inclusions on the wall, inside the submerged entry nozzle [6]. As the authors comment, attempts to compensate the problem by further opening the metering nozzle controlling the steel flow from tundish to mold would not lead to a final solution as the deposited inclusions could break from the nozzle wall and remain in the solidifying slab as macroinclusions.

The application of *calcium treatment* to improve the castability of Al-killed steels– after being introduced as a deep desulphurization treatment in the 1970s – created a new paradigm and became awell-established practice in the 1980s [5, 7, 8, 9]. Briefly, it consists in the modification of solid Al_2O_3 inclusions to calcium aluminates which are *liquid* at casting temperatures and should not cause deposits on the nozzle wall. In practice, due to the presence of sulfurinmolten steel, the chemistry may change a little –aside from liquid 'CaO-Al_2O_3-CaS' inclusions, also solid CaS can form. As Holappa and co-workers explain in their research article, the search for the adequate thermodynamic conditions is conducted using for the calculations a steel grade with the composition: 0.35%C, 0.25%Si and 0.50%Mn. The limits of the area where only liquid aluminates can be found(reminding roughly a *triangle* in a diagram depicting the Al and Ca content as axis) were determined by calculating the saturation lines of (i) solid calcium aluminates ($CaO{\cdot}Al_2O_3$, $CaO{\cdot}2Al_2O_3$) and (ii) solid CaS, respectively. The necessary calcium addition – as a function of some previously

fixed aluminum content – was determined by an iteration method to find each saturation. Their results show the effect of oxygen and sulfur content on the limits of formation of liquid calcium aluminate inclusions as a function of temperature; as the authors point out, the performance of this 'liquid window' is strongly related to nozzle clogging problems in continuous casting of steels (Al content was kept higher than 100 ppm – up to 400 ppm –since, at very low values, Ca-Al silicates are formed, closing the 'triangular window').
Based on their study, some research papers using asimilar technique to determine the 'liquid window' were published, mainly focusing on SAE 8620 steel [10, 11, 12, 13].
Since that 2003 article [5], thermodynamic software as well as thermodynamic data, concerning liquid steel and liquid slag, experienced an appreciable development. Not only this, but especially graphics capabilities of the modern thermodynamic packages, available for results visualization, have had a great evolution – accompanying the general trend observed in the computer industry's recent history**.** Concerning the displaying of results, one can find today, as standard features in software packages, some very useful–so to speak–'graphic result modules' with capabilities ranging from graphical presentation of standardized, universally accepted diagrams like 'Pourbaix diagrams' or 'predominance area' diagrams, up to more flexible, adjustable 'phase diagrams', able to suit a variety of particular tasks.
Last but not least, it should be emphasized that 'inclusion engineering' area is a complex subject; the support of material thermodynamics is important for understanding, though, it is not enough to alone fully explain the reasons for the submerged entry nozzle clogging.
Aim of the present work is, to some extent, to repeat the fundamental part of the computational calculations made by Holappa *et al.*,(taking the same steel grade),making use of a modern thermodynamic software and databases, this time plotting the graphic results *directly* from the software, in order to visualize the relevant thermodynamic conditions suggested by those authors as a means to minimize the SEN clogging. The intention of stimulating students at the undergraduate level to include computer assisted thermodynamics in their studies fulfills the remaining part of this work's objective.

2 DEVELOPMENT

Thermodynamic theoretical calculations to find the uncertain boundaries of the 'liquid window' (region containing only *liquid* oxide phase in equilibrium with liquid steel)were carried out using a steel with the(fixed)chemical composition:0.35%C, 0.25%Si and 0.50%Mn.The 'margins' of the 'liquid window', limited to the system Fe-Al-Ca-O-S, are modified to some extent by oxygen, sulfur and aluminum content, as well as by the temperature. Limits for the variables are: 20-30ppm O,50-250 ppm S, 100-400ppm Al, and 1550-1600 °C for the temperature.
The thermodynamic-based study was carried out using the commercial software suite FactSage and its databases (both from GTT and FACT groups).The results are phase diagram splotted as a function of the composition (usual axes: Al as a function of Ca or O content), at a fixed temperature.
To enhance the limits of the 'liquid window' and facilitate the identification it is colored in blue; for the sake of simplicity, other phase fields are not labeled in this study.

3 RESULTS AND DISCUSSION

In the first series of calculations the influence of sulfur and temperature on the limits of the 'liquid window' was examined; to eliminate the influence of oxygen, its content was kept constant at 20 ppm. Two different temperatures and two levels of total sulfur content in the system were 1550 and 1600 °C, and 50 and 250 ppm, respectively.

It is observed that under the conditions of 50 ppm S and 1600 °C, the liquid window extends over a large area, **Figure1**. This demonstrates that the chosen conditions are somewhat favorable so that the casting of the steel occurs without the disturbing threat of nozzle clogging.

Rising five times the initial sulfur content, from 50 to 250 ppm, there is a reasonable reduction in the size of the liquid window, **Figure2**. Although smaller than the previous one, the new 'liquid window' still shows a relatively favorable situation, which can be associated with a moderate risk of nozzle clogging.

Returning to the initial conditions of 50 ppm S, but lowering the temperature to 1550 °C, the situation changes little in relation to the last seen case (1600 °C with 250 ppm S), **Figure3**. However, with the two adverse conditions occurring at the same time – 250 ppm sulfur content at 1550 °C – there is a noticeable reduction of the 'liquid window', **Figure4**. This fact highlights the strong influence that sulfur exerts at low temperatures – precisely the condition found at the moment the steel approaches its solidification.

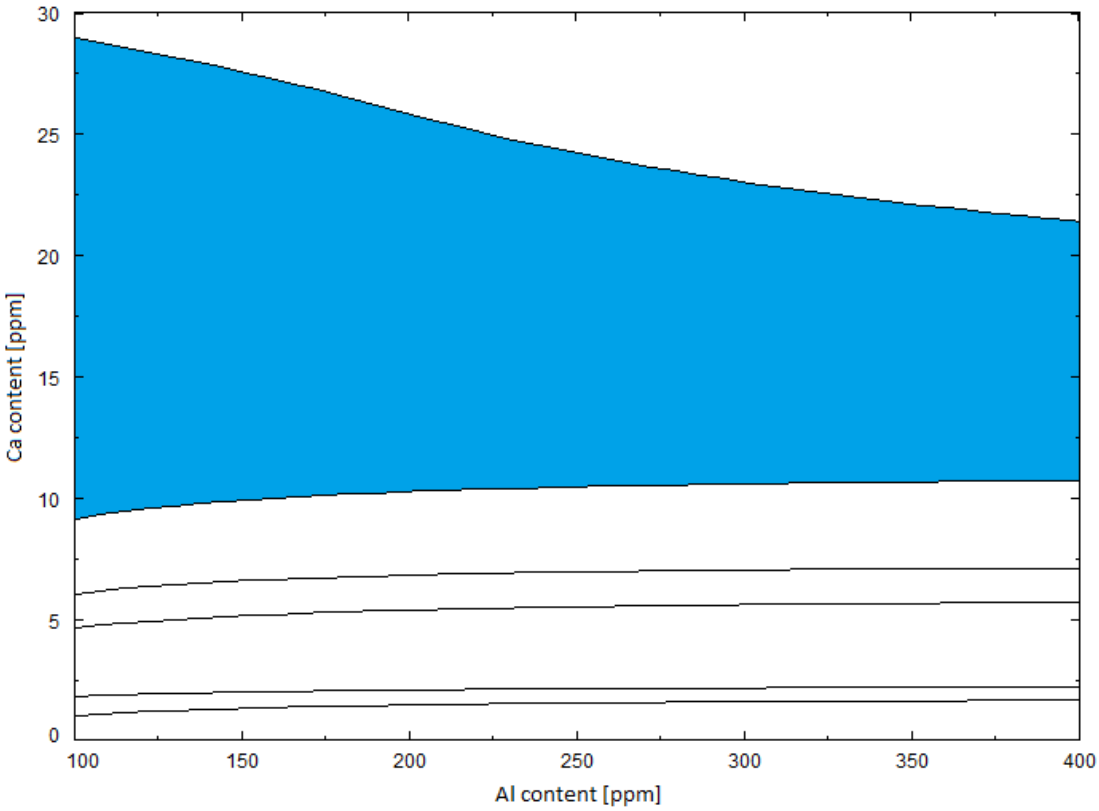

Figure 1. Effect of sulfur in the 'liquid window' (in blue): 50 ppm S, 20 ppm O, 1600°C

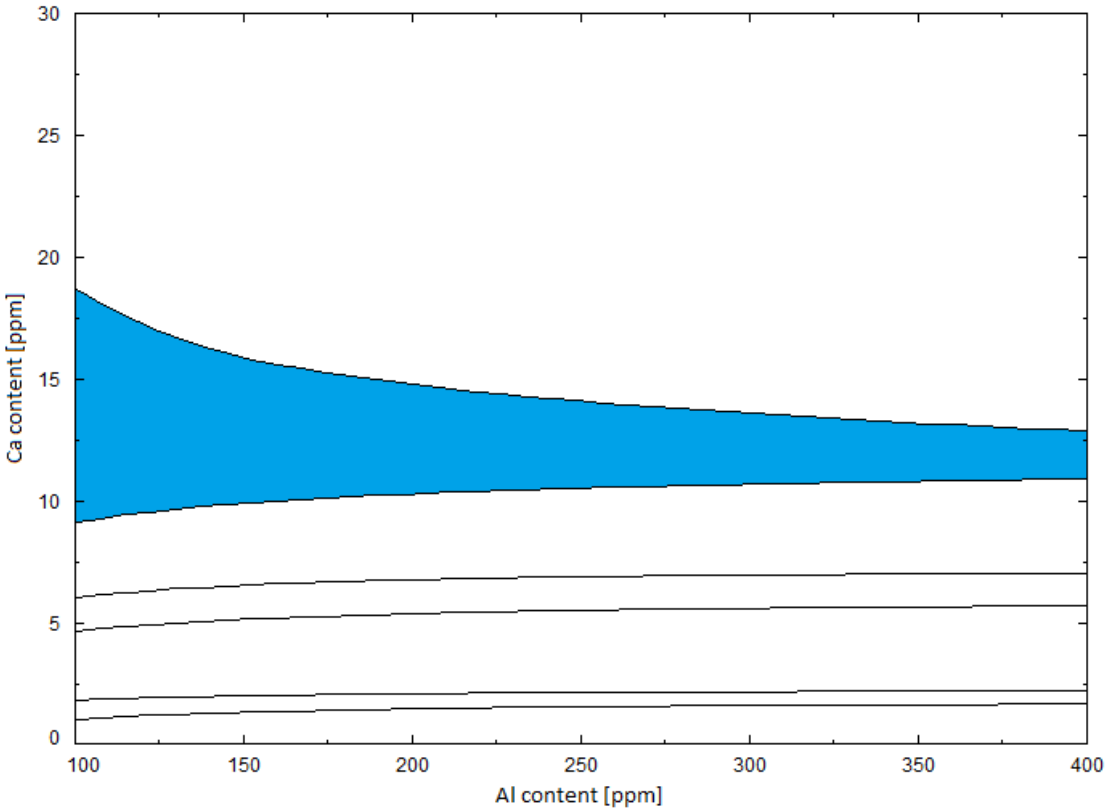

Figure 2. Effect of sulfur in the 'liquid window' (in blue): 250 ppm S, 20 ppm O, 1600°C

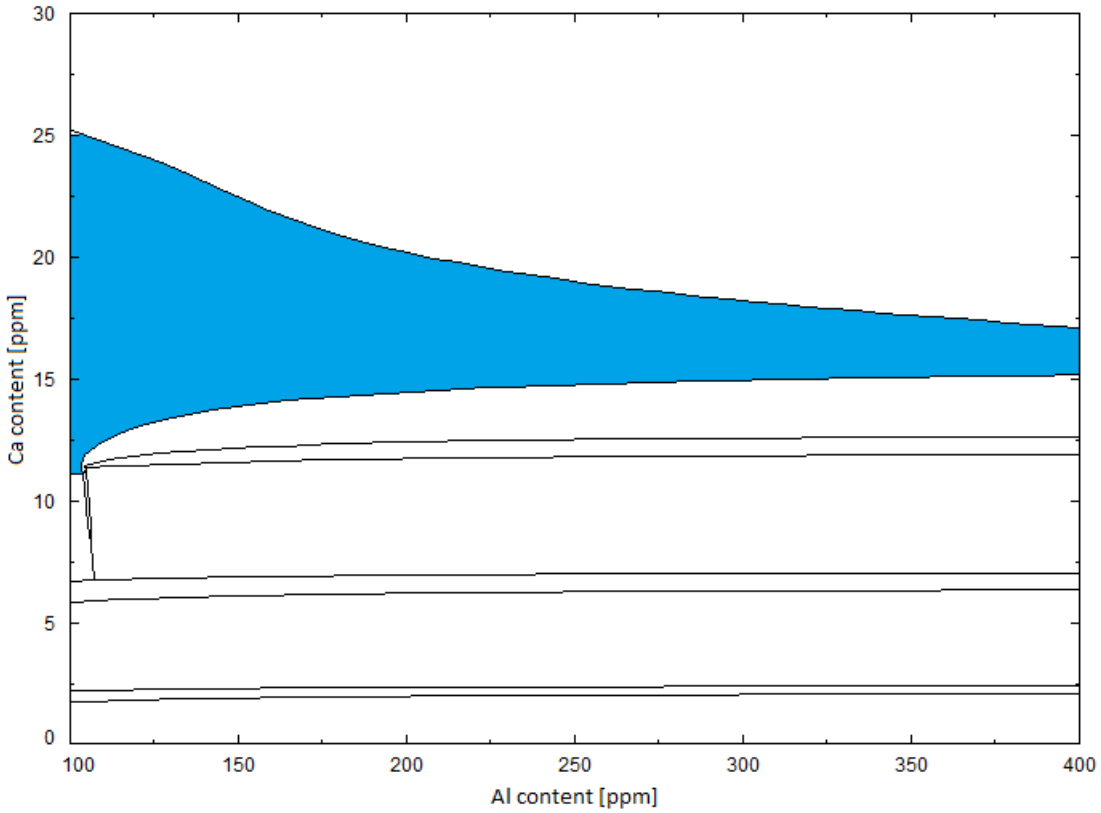

Figure 3. Effect of sulfur in the 'liquid window' (in blue): 50 ppm S, 20 ppm O, 1550°C

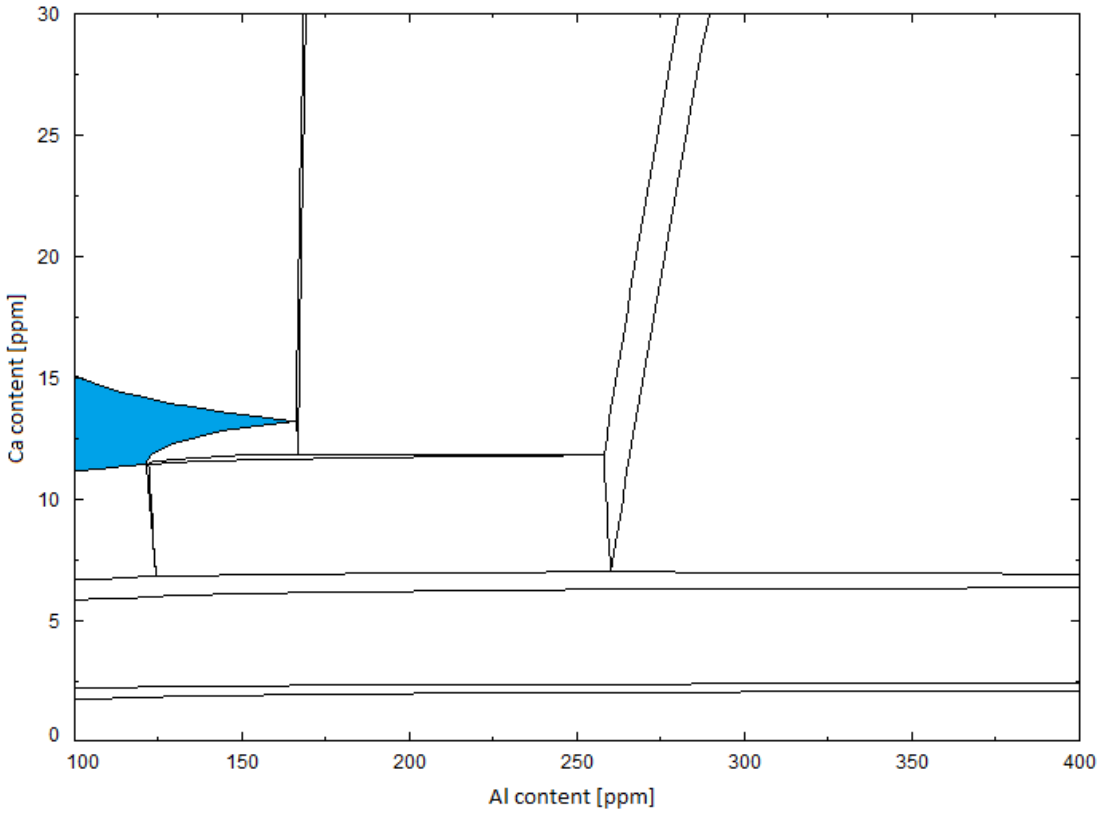

Figure 4. Effect of sulfur in the 'liquid window' (in blue): 250 ppm S, 20 ppm O, 1550°C

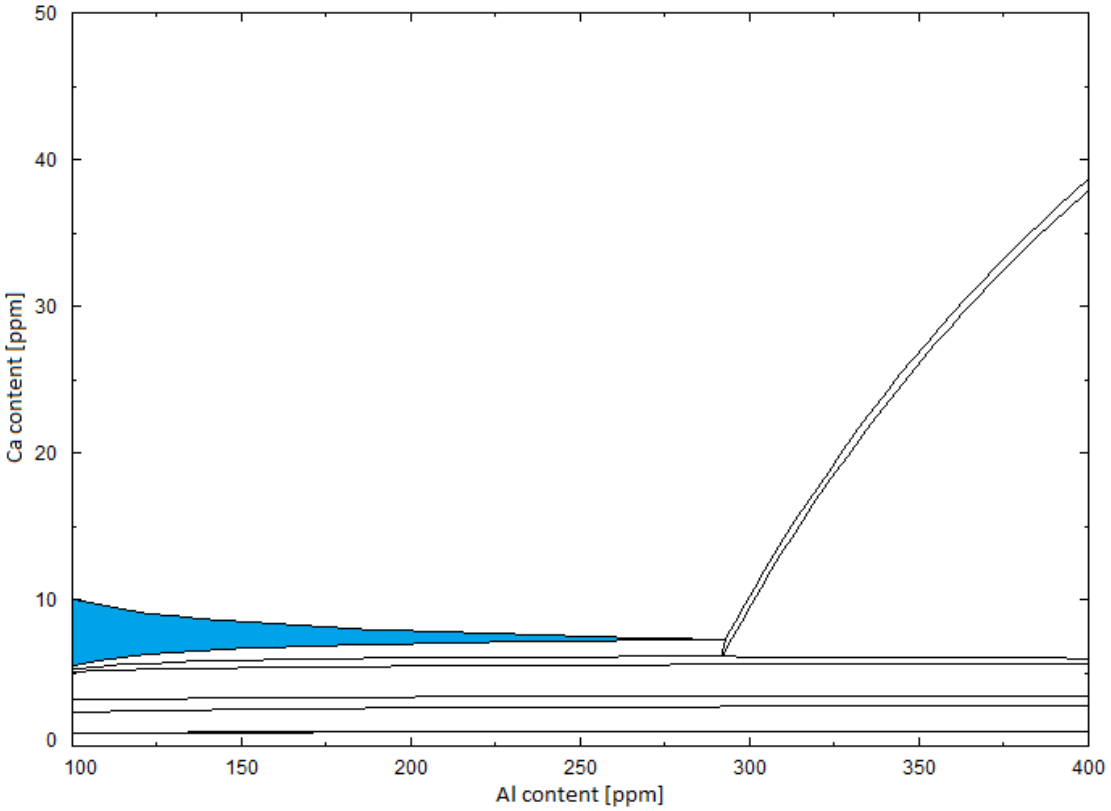

Figure 5. Effect of oxygen in the 'liquid window' (in blue): 10 ppm O, 100 ppm S, 1550°C

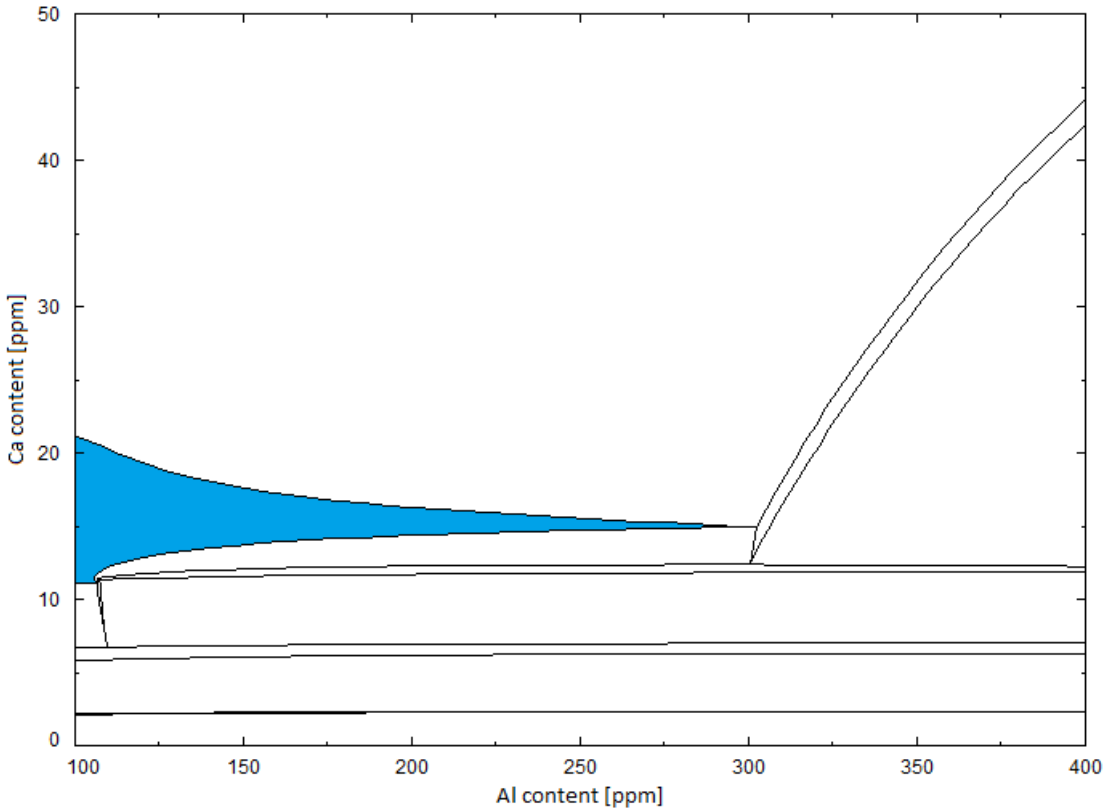

Figure 6. Effect of oxygen in the 'liquid window' (in blue): 20 ppm O, 100 ppm S, 1550°C

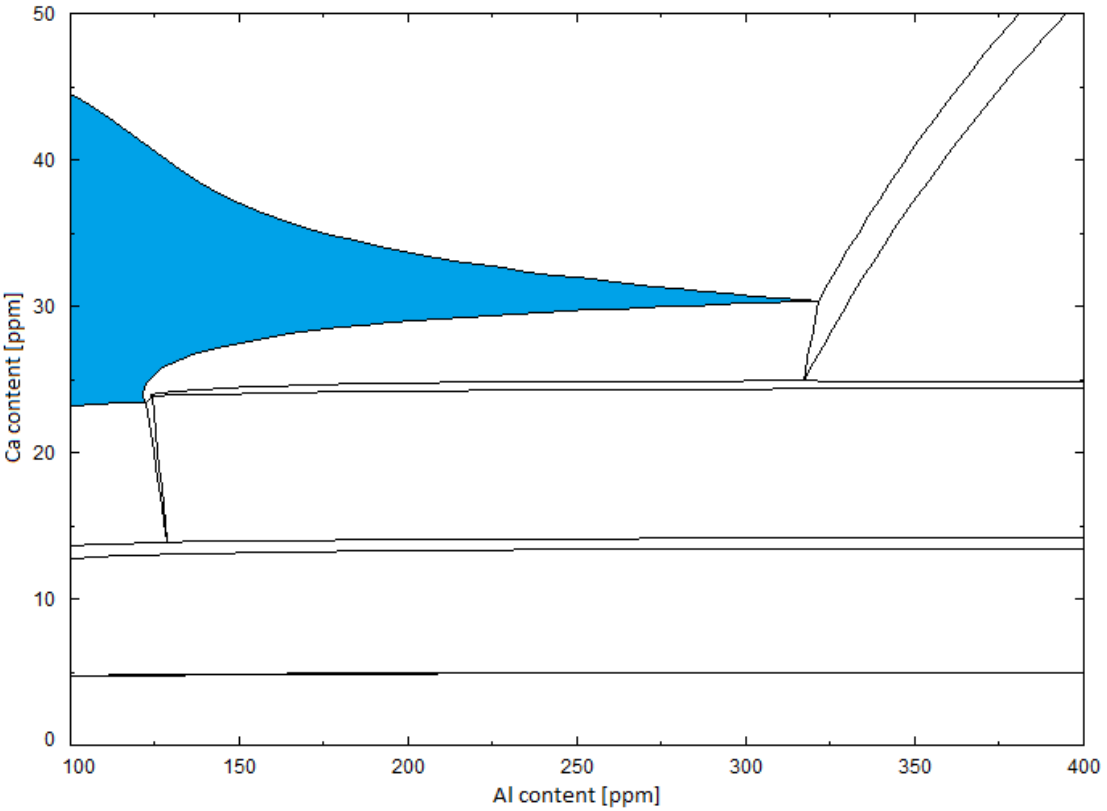

Figure 7. Effect of oxygen in the 'liquid window' (in blue): 40 ppm O, 100 ppm S, 1550°C

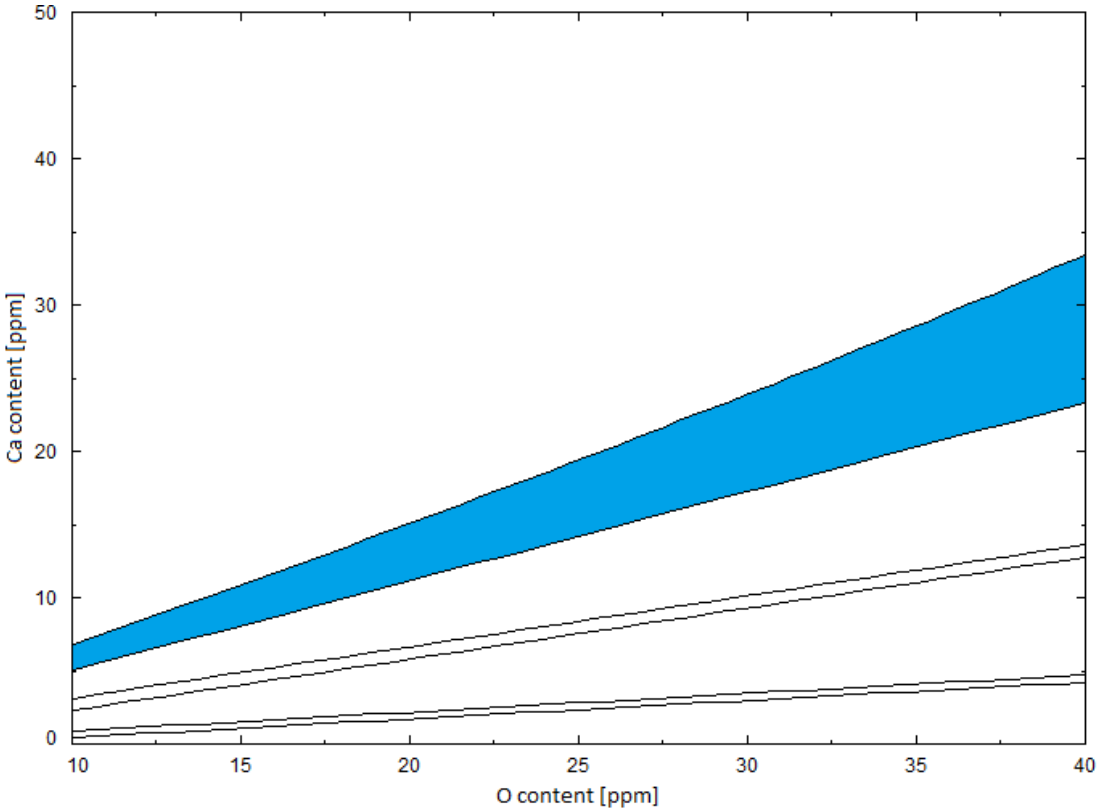

Figure 8. Profile of the 'liquid window' (in blue): 100 ppm Al, 250 ppm S, 1550°C

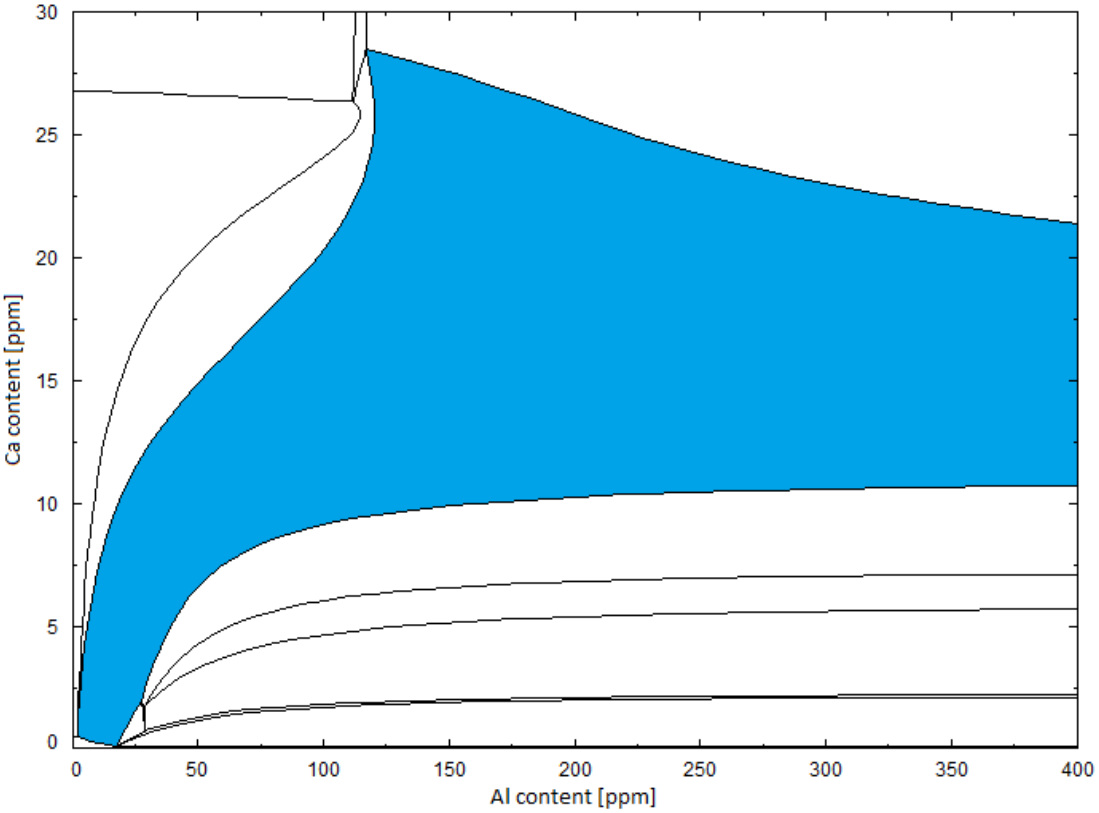

Fig.9. 'Full' view of the'liquid window' (in blue): 20 ppm O, 250 ppm S, 1600°C

The influence exerted by the oxygen on the 'liquid window' will be examined in a second series of simulations. For these calculations the sulfur was kept constant at 100 ppm S, and the temperature at 1550 ° C. Three sections showing the liquid window were made at 10, 20 and 40 ppm O, **Figures5**, **6** and **7**. It is easy to verify that a lower oxygen content results in a narrow 'liquid window' with an upper limit of 10 ppm of calcium. As the oxygen content increases, it moves upward and the width of the window also increases.

A longitudinal cut, made with an Al content of 100 ppm, but with a moderately high content of S and a temperature of 1550 ° C – to simulate unfavorable conditions – can be seen in **Figure8**. The same general characteristics seen in **Figures5**, **6** and **7** can be identified in this profile; *i.e.* as a function of the oxygen content, the liquid window moves to a region of higher Ca levels and its width becomes larger – disfavoring the occurrence of nozzle clogging.

Holappa *et al.* [4] draw attention, in their work, to the fact that at very low aluminum contents the window 'closes' because of the precipitation of Ca-Al silicates. This suggestion served as motivation for a last simulation: under conditions of 20 ppm O, 250 ppm S, and temperature of 1600 °C, the results fully confirmed the prediction – as can be seen in **Figure 9**.

4 CONCLUSIONS

Considering the results of the simulations it can be said that the following factors tend to favor the appearance of nozzle clogging: low oxygen contents; high levels of sulfur; and, lower temperatures.

As expected, these conclusions are in agreement with those obtained by Holappa *et al.* in their article highlighting the influence of process factors on the 'liquid window'.

It can also be emphasized that the facilities provided by the possibility of plotting the results of software calculations, without the need for iterative, exhaustive computations, one for each of the points examined, greatly favor the analysis of the essential conditions needed for the production of quality steels.

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